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CHEMICAL REACTION SYSTEMS SENSITIVITY
STUDY

J. H. Schaibly

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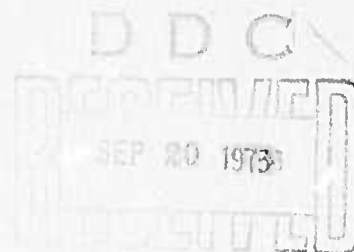
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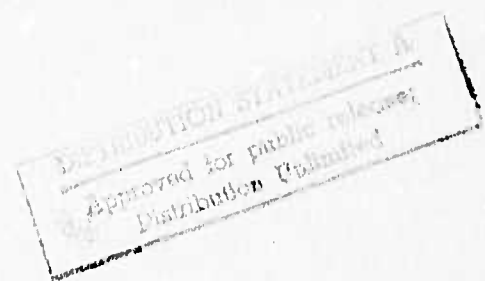
INTRODUCTION

This report constitutes a Semi-Annual report for contract N00014-73-C-0270 administered by the office of Naval Research. The research is being carried out at Systems, Science and Software. (S^3)

The research performed under this contract is a continuation of work begun under a previous contract at S^3 to investigate methods for determining the sensitivity of the results of complex calculations to uncertainties in the modeling parameters entering the calculations. The emphasis to date has been concentrated on non-equilibrium chemical kinetics systems, to determine the sensitivity of calculated concentrations to experimental uncertainties in the rate coefficients.

In the previous contract, a method called the Fourier Amplitude Sensitivity Test (FAST) was developed and applied to two simple chemical systems. It was shown that the method does provide a measure of the relative contribution from each rate constant uncertainty to the uncertainty of the calculated concentrations.

The present research effort is just getting under way, and consists in applying FAST to two particular chemical kinetics problems of interest to the high altitude fireball community. Results from this work will be available soon.

The work that was done in the previous contract has recently been written up in two companion papers which have been accepted by the Journal of Chemical Physics for publication. Preprints of these two papers are included as the remainder of this report.

A STUDY OF THE SENSITIVITY OF COUPLED REACTION

SYSTEMS TO UNCERTAINTIES IN RATE COEFFICIENTS

I. THEORY [‡]

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ABSTRACT

A method has been developed to investigate the sensitivity of the solutions of large sets of coupled, non-linear rate equations to uncertainties in the rate coefficients. This method is based on varying all the rate coefficients simultaneously through the introduction of a parameter in such a way that the output concentrations become periodic functions of this parameter at any given time t. The concentration of the chemical species are then Fourier analysed at time t. We show via an application of Weyl's ergodic theorem that a subset of the Fourier coefficients is related to $\left\langle \frac{\partial c_i}{\partial k_\ell} \right\rangle$, the rate of change of the concentration of species i with respect to the rate constant for reaction ℓ averaged over the uncertainties of all the other rate coefficients. Thus a large Fourier coefficient corresponds to a large sensitivity, a small Fourier coefficient corresponds to a small sensitivity. The amount of numerical integration required to calculate these Fourier coefficients is considerably less than that required in tests of sensitivity where one varies one rate coefficient at a time, while holding all others fixed. The Fourier method developed in this paper is not limited to chemical rate equation, but can be applied to the study of the sensitivity of any large system of coupled, non-linear differential equations with respect to the uncertainties in the modeling parameters.

I. Introduction

Sets of coupled, non-linear rate equations arise in a number of disciplines. A classic example is that of chemical rate equations. In the study of combustion, air-pollution, upper atmosphere phenomena and chemical lasers as many as 100 coupled rate equations involving some 50 separate species may be needed to account for the properties of such systems. One is then faced with the problem of solving a large set of coupled, non-linear differential equations of the form

$$\frac{d\vec{c}}{dt} = \vec{F}\left[\vec{c}_i\{k\}\right] \tag{1.1}$$

when $\vec{c}$ is a vector of concentrations, $\{k\}$ a set of rate coefficients and $\vec{F}$ some complicated function of the concentrations. While one may prove existence and stability theorems for the equilibrium point[1], the only way to solve these equations, i.e. to obtain all the species concentrations as functions of time, is through the use of a high-speed computer.

Unfortunately, the rate coefficients (or cross sections) for many reactions are not known with high accuracy and indeed may be uncertain by one or more orders of magnitude. This gives rise to the very important problem of "sensitivity" which may be defined as the effect of uncertainties in the rate coefficients on the calculated concentrations of all the various intermediate and product species. The uncertainty in the rate coefficients of certain "important" reactions in the reaction scheme may have a significant effect on the output function (for instance, concentration at time t), while uncertainties of the same magnitude in rate coefficients of "unimportant" reactions in the reaction scheme may hardly effect the output function. The reliability of the

output numbers clearly cannot be established without knowledge of the sensitivity of the output data to the uncertainty in the input parameters.

The problem is to find a practical method of determining the effects of the uncertainties in the rate coefficients on the solutions of the rate equations. Since we are interested in the situation where the uncertainties in the rate coefficient may be orders of magnitude, linearization schemes are not appropriate. A "brute force" method of investigating the sensitivity is not feasible as can readily be seen from the following example. Suppose we have a reaction scheme which has n coupled reactions involving m different chemical species. Let us furthermore assume that we wish to calculate the concentrations of the m species at some time t for z different values each of the 2n rate coefficients. If we now change one rate coefficient at a time while holding all the others fixed, we would have to carry out z^{2n} integrations of the rate equation (1.1) to time t. For the m different species, this procedure will give rise to a print-out of $m(z)^{2n}$ concentrations. If we know to a good accuracy the equilibrium constants for all the reactions and apply the principle of detailed balance, the number of independent rate coefficients will be reduced to n and we would have to carry out z^n integrations up to time t for each species m. In either case, for n large, it is obvious that the time and expense involved in such an analysis of sensitivity is prohibitive and the print-outs so numerous as to defy a simple analysis of the results. Clearly, one needs to devise some more powerful method for the study of sensitivity.

Our approach to this problem is to ask for a less detailed description of the effect of rate coefficient uncertainty on the output function at any given time. We vary all the rate coefficients simultaneously so as to explore the

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entire space of uncertainties in the rate coefficient set {k}. As will be seen below, this turns out to be equivalent to varying a single rate coefficient and then averaging the attendant concentration changes over the uncertainties of all the other rate coefficients, where we express this uncertainty in terms of a probability distribution. Our approach is thus related to a "mean field" theory where we represent the fluctuations of the field by the uncertainties in the (n-1) rate coefficients over which we average.

To carry out this program, we relate each rate coefficient k_i to a frequency ω_i and introduce a parameter s which simultaneously varies all the rate coefficients in such a way that the concentrations <u>at a fixed time</u> become periodic functions of s. The concentrations can then be Fourier analyzed. We then show that a certain subset of these Fourier coefficients can be related to the first partial derivative of the concentration c_i of species i with respect to a rate coefficient k_ℓ averaged over the uncertainties of all the other rate coefficients. A large value of the Fourier coefficient $A_{\omega_\ell}^{(i)}$ then shows that $\left\langle \frac{\partial c_i}{\partial k_\ell} \right\rangle$ is large, i.e. the effect of a change in the ℓ'th rate coefficient on the concentration of species i is significant. Conversely, a small Fourier coefficient $A_{\omega_j}^{(i)}$ indicates that $\left\langle \frac{\partial c_i}{\partial k_j} \right\rangle$ is small, i.e. the effect of the variations of the j'th rate coefficient on the concentration of species i is small. In order to calculate these Fourier coefficients, we must integrate the rate equations numerically up to the desired time for each value of the parameter s. The number of s values which we include in our parameter set determines the accuracy to which we can calculate the Fourier coefficient; the larger the set of s values, the more accurate the determination of the Fourier coefficients.

Since we must still perform numerical integrations of the rate equations

(1.1), the question arises why this method is to be preferred to the more direct method of varying each rate coefficient separately while keeping all others fixed. As will be shown in paper II, which deals primarily with the computer calculations, the number of integrations required by the Fourier method is $O(n^r)$ where r is a small integer ($r<10$) which depends upon the choice of the frequencies ω_i, $i = 1,2,\ldots,n$. It can readily be verified that for n, z large, $n^r<(z)^n$. The computational economy of this method of analysis thus becomes more pronounced as n, the number of reactions, increases. The reason for this reduction in the number of required integrations up to time t is to be found in the fact that in the Fourier method we <u>sample</u> the $\vec{c}(k)$ space at a set of points determined by the values of the set $\{s\}$ and the vector $\vec{\omega}$, whereas the "brute force" method involves neither sampling nor the simultaneous variation of the set of rate coefficients $\{k\}$ and thus requires many more integrations of the rate equations. As will be clear from the body of the paper, this sampling in a certain sense corresponds to the averaging over all the rate coefficients. The reduction in the number of required integrations is thus intimately related to the use of a "mean field" theory.

Our results are presented in two papers, I and II. In paper I, we present the theoretical basis of our method without explicit reference to the verifying computer experiments. In paper II, we present the results of our computer calculations as well as a detailed discussion of the problems involved in such calculations.

It should be pointed out that the utility of this Fourier analysis method of testing sensitivity extends beyond the confines of chemical kinetics and beyond the confines of differential equations. Large sets of coupled, non-linear equations are used in many fields such as economics, population dynamics, weather forecasting, systems analysis, operations research, etc. for modeling

and predictive purposes. As has been pointed out by a number of investigators, it is important that sensitivity tests be carried out on such systems to identify the critical parameters and to validate the applicability of the models. The method developed here can be applied to any set of equations, differential, integral, algebraic, etc., which yield an output as a complex function of many parameters. In fact, we have used an analytic function of several variables to test some of our ideas. We plan to apply this Fourier method to the analysis of other complex systems in the near future.

II. Fourier Analysis

The rate equation for coupled chemical reactions which obey the law of mass action can be written in the form

$$\frac{dc_i}{dt} = \sum_{r=1}^{n} \nu_{r,i} \left[k_r \prod_{\ell=1}^{m} c_\ell^{\nu'_{r,\ell}} - k_{-r} \prod_{\ell=1}^{m} c_\ell^{\nu''_{r,\ell}} \right] \qquad (2.1)$$

$$(i=1,\ldots,m)$$

where $c_i(k_1,\ldots,k_n;t)$ is the concentration of species i at time t, $\nu_{r,i} \equiv \nu''_{r,i} - \nu'_{r,i}$ is the stoichiometric coefficient of the species i in reaction r, with $r=1,\ldots,n$ labeling the different reactions in the reaction system, and where $k_r (k_{-r})$ is the forward (backward) rate coefficient for reaction r. The coefficients $\nu'_{r,i}$ and $\nu''_{r,i}$ are non-negative integers so that the stoichiometric coefficient ν_{ri} defined above can be positive, negative or zero. From the form of the rate equations (2.1) one can prove that the concentrations are bounded and non-negative, that they are continuous functions of the time and the rate coefficients and that an equilibrium point exists.[1]

In order to determine the effects of uncertainties in the rate coefficients $k_{\pm r}$ on the concentrations c_i at time t a systematic method for varying the k's must be developed. We define

$$k_i = k_i^{(o)} e^{u_i} \qquad (i=1,\ldots,m) \qquad (2.2)$$

and

$$u_i = f_i(\sin \omega_i s) \qquad (2.3)$$

where $k_i^{(o)}$ is the "best value" of the rate coefficient (i.e. the one which the investigator believes to be the best available value based on experiments or calculations), the "frequency" ω_i is a positive integer, s is a parameter and f_i

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is a function to be determined. The introduction of the parameter u_i and the form of Eq. (2.2) permits one to effect readily order of magnitude changes in the rate coefficients. The form of equation (2.3) permits one to vary simultaneously all the rate coefficients by varying the parameter s. The rapidity of the variation is determined for each k_i by the magnitude of the ω_i's. The ω_i are chosen to be positive integers in order that the concentrations at a fixed time t become periodic functions of s with period 2π:

$$c_i(s;t) = c_i(s + 2\pi;t) \tag{2.4}$$

In the development to follow we suppress this dependence of the concentrations on time, it being understood that the analysis is carried out for a fixed time t.

The concentration as a function of s describes a closed path. That is, for each i and for every value of s we obtain a point in $\vec{k}$ space with value $c_i(\vec{k})$; as s changes by 2π we return to the same values of $\vec{k}$ and $\vec{u}$, [see eqs. (2.2) and (2.3)], and, from equation (2.4), to the same value $c_i(s)$. Since $c_i(s)$ is periodic on 2π we may expand it in a Fourier series

$$c_i(s) = \frac{A_0^{(i)}}{2} + \sum_{r=1}^{\infty} \left(A_r^{(i)} \sin rs + B_r^{(i)} \cos rs \right) \quad . \tag{2.5}$$

In the analysis presented below we are interested only in the Fourier sine coefficients A_r that correspond to the original input frequencies ω_i, i.e. the coefficients given by

$$A_{\omega_\ell}^{(i)} = \frac{1}{\pi} \int_0^{2\pi} c_i(s) \sin \omega_\ell s \, ds \quad . \tag{2.6}$$

$$\ell = 1,2,\ldots,n$$

We now wish to relate the Fourier coefficients $A_{\omega_\ell}^{(i)}$ to the effect of the

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variation of the rate coefficients k_r and the concentrations c_i. In order to do this it is necessary to relate the s- space integral of Eq. (2.6) to a n-dimensional integral over the entire $\vec{u}$ space. It can be shown that if the entire $\vec{u}$ space is covered densely as s is varied, then the integrals over the s- space and the $\vec{u}$ space yield identical results. This is just a statement of the ergodic theorem which permits one to equate time and phase space averages in statistical mechanics.[2] If the frequencies ω_i in Eq. (2.3) were chosen to be incommensurate, then the function $c_i(s)$ i.e. the concentration as a function of the parameter s, would be an almost periodic function. This implies that the path in the space $R^n(\vec{\theta})$, where the θ's are defined by

$$\theta_i = \omega_i s \qquad (\text{mod } 2\pi) \tag{2.7}$$

returns arbitrarily close to any initial point as $s \longrightarrow \infty$. One could then equate the s- space integral with the integral over the n- dimensional $\vec{\theta}$ space as was first proved by Weyl.[3] However, the use of an incommensurate set of frequencies ω_i in Eq. (2.3) would require that the numerical evaluation of the Fourier coefficients A_{ω_ℓ} of Eq. (2.6) be carried out over an infinite period. This clearly is not a feasible procedure on any known computer.

It is for this reason that we introduce integer frequencies ω_i in Eq. (2.3). Their use leads to a finite period (0 to 2π) analysis which can readily be handled on a computer. This will give rise to an error in the analysis since now the "phase point" will no longer densely cover the $\vec{u}$ space as s is varied and the s-space and $\vec{u}$ space integrals therefore do not yield identical results.

Let us for the moment ignore this error and use Weyl's theorem for our periodic function c(s). We write

$$A_{\omega_\ell}^{(i)} = \frac{2}{(2\pi)^n} \int_0^{2\pi} \cdots \int_0^{2\pi} \prod_{j=1}^{n} d\theta_j \, c_i(\theta_1,\ldots,\theta_n) \sin \theta_\ell \qquad . \tag{2.8}$$

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This expression can be put in a more suggestive form as follows. The ℓ'th integral is rewritten by integration by parts as

$$\frac{1}{2\pi} \int_0^{2\pi} d\theta_\ell \; c(\theta_1 \ldots \theta_n) \sin \theta_\ell = \frac{1}{2\pi} \int_0^{2\pi} d\theta_\ell \; \frac{\partial c}{\partial \theta_\ell} \cos \theta_\ell \qquad (2.9)$$

where the boundary term has vanished by the periodicity of the integrand. The use of Eq.(2.9) then permits us to rewrite Eq.(2.8) as

$$A_{\omega_\ell}^{(i)} = \frac{2}{(2\pi)^n} \int_0^{2\pi} \cdots \int_0^{2\pi} \prod_{j=1}^{n} \; d\theta_j \; \frac{\partial c_i}{\partial \theta_\ell} \cos \theta_\ell \qquad (2.10)$$

The $\vec{\theta}$ space integral must now be related to the $\vec{u}$ space integral. The transformation is (see Eqs. (2.3) and (2.7))

$$du_j = \frac{\partial f_j(\sin \theta_j)}{\partial \sin \theta_j} \cos \theta_j \; d\theta_j \qquad (2.11)$$

where we require that f_j be a monotonic function of its argument. Then

$$A_{\omega_\ell}^{(i)} = \frac{2}{\pi^n} \int_{f_1(-1)}^{f_1(+1)} \cdots \int_{f_n(-1)}^{f_n(+1)} \frac{\displaystyle\prod_{j=1}^{n} du_j \cos \theta_\ell \frac{\partial c_i}{\partial u_\ell}}{\displaystyle\prod_{j \neq \ell}^{n} \cos \theta_j \frac{\partial f_j(\sin \theta_j)}{\partial \sin \theta_j}} \qquad (2.12)$$

In order to obtain a definite relation between $A_{\omega_\ell}^{(i)}$ and $\partial c_i/\partial u_\ell$ we must choose some particular form for the function $f_j(\sin \theta_j)$. There are several choices which lead to useful expressions for the $A_{\omega_\ell}^{(i)}$; as will be seen below, a particularly advantageous choice is to set

$$\frac{\partial f_j(\sin \theta_j)}{\partial \sin \theta_j} \cos^2 \theta_j = \frac{1}{a_j} \; , \qquad (2.13)$$

where a_j is a parameter. The use of Eq. (2.13) in Eq. (2.12) leads to

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$$A_{\omega_\ell}^{(i)} = \frac{2}{a_\ell \pi^n} \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} \prod_{j=1}^{n} du_j \, a_j \cos \theta_j \frac{\partial c_i}{\partial u_\ell} \quad . \tag{2.14}$$

Integration of Eq. (2.13) yields

$$f_j(\sin \theta_j) = u_j = \frac{1}{2a_j} \ell n \left[\frac{1 + \sin \theta_j}{1 - \sin \theta_j} \right] \tag{2.15}$$

and also indicates the range of integration in Eq. (2.14). Expressing $\cos \theta_j$ as a function of u_j from Eq. (2.15) gives for Eq. (2.14)

$$A_{\omega_\ell}^{(i)} = \frac{2}{a_\ell \pi^n} \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} \prod_{i=1}^{n} du_j \, \frac{a_j}{\cosh a_j u_j} \frac{\partial c_i}{\partial u_\ell} \quad . \tag{2.16}$$

Since

$$\int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} \prod_{j=1}^{n} du_j \, \frac{a_j}{\cosh a_j u_j} = \pi^n \tag{2.17}$$

we obtain as our final result

$$A_{\omega_\ell}^{(i)} = \frac{2}{a_\ell} \langle \partial c_i / \partial u_\ell \rangle \tag{2.18}$$

where the bracket in Eq. (2.18) is defined by

$$\langle Y(u_1, \ldots, u_n) \rangle = \frac{\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{+\infty} \prod_{j=1}^{n} p(u_j; a_j) \, Y(u_1, \ldots, u_n) \, du_j}{\int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} \prod_{j=1}^{n} p(u_j; a_j) \, du_j} \tag{2.19}$$

and

$$p(u_j; a_j) = \frac{a_j}{\cosh a_j u_j} \quad . \tag{2.20}$$

The function $p(u_j; a_j)$ can be interpreted as a distribution function in $\vec{u}$ space which weights the uncertainty in the rate coefficients. Equation (2.18) is the

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desired relation between the Fourier coefficient $\Lambda_{\omega_\ell}^{(i)}$ and the change in the concentration of species i with a change in the ℓ'th rate coefficient, $\partial c_i/\partial u_\ell$, averaged over the changes of all the other rate coefficients.

The particular form of f_j (sin θ_j) that we have chosen, Eq. (2.15), has lead to a weight function $p(u_j;a_j)$ for each rate coefficient, Eq. (2.20), which has several convenient properties. As a function of u_j, the function $p(u_j;a_j)$ is symmetrically bell shaped about $u_j=0$ corresponding to $k_j=k_j^{(0)}$, the "best" value of the rate coefficient k_j. As a_j, which is a parameter at our disposal, is increased, the weight function $p(u_j;a_j)$ narrows about $u_j=0$; this corresponds to a decreased spread in the values of the rate constant k_j, i.e. it corresponds to a narrower range of the uncertainty of k_j around $k_j^{(0)}$. In the limit as $a_j\to\infty$, one obtains

$$\lim_{a_j\to\infty} p(u_j;a_j) = \pi\delta(u_j) \tag{2.21}$$

where $\delta(x)$ is the delta function of argument x which implies that the rate constant is known with certainty to be $k_j^{(0)}$. When some information is available on the spread and distribution of the rate coefficient k_j about its "best" value $k_j^{(0)}$, one can determine the a_j through the standard deviation of the values in $\vec{u}$ space

$$\langle u_j^2 \rangle = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{u_j^2\, a_j\, du_j}{\cosh a_j u_j} = \frac{\pi}{4}\ \frac{1}{a_j^2} \tag{2.22}$$

from which it follows that

$$a_j = \frac{\pi}{2}\ \frac{1}{\langle u_j^2 \rangle^{1/2}} \qquad . \tag{2.23}$$

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The parameter a_j thus permits us to introduce explicitly the spread of uncertainties in the values of the rate coefficients into our analysis.

To calculate the Fourier coefficients $A_{\omega_\ell}^{(i)}$ we must first choose a suitable set of ω_j's and a_j's. What constitutes a "suitable" set of ω's will be discussed in the next section in conjunction with the error analysis and in more detail in paper II. The set of ω_j's defines the u_j's as a function of s according to Eqs. (2.3), (2.7) and (2.15). For each value of s one obtains a value of the concentration $c_i(k_1,...,k_n)$. In principle one can then compute the $A_{\omega_\ell}^{(i)}$ to any desired accuracy by taking enough values of s,

$$s = \frac{2\pi q}{m} , \quad q = 1,2,...,m, \tag{2.24}$$

where m is some integer.

It is important to point out that our main interest is in identifying those rate coefficients whose variation significantly effects the concentration c_i of a species i at time t, and those rate coefficients whose variation has only a minimal effect on the species concentration c_i. Thus if one of the Fourier coefficients, say $A_{\omega_j}^{(i)}$, is one or more orders of magnitude larger than all other coefficients $A_{\omega_\ell}^{(i)}$, $\ell = 1,2,...,n$, $(\ell \neq j)$, than the variation of the j'th rate coefficient k_j, clearly has a larger effect on the concentration $c_i(t)$ than the variation of the other rate coefficients. If on the other hand all the coefficients $A_{\omega_\ell}^{(i)}$, $\ell = 1,2,...,n$, are of the same order or magnitude, then the concentration of species i at time t, $c_i(t)$, is effected essentially equally by the variation of any of the rate coefficients k_ℓ.

One problem with the above analysis must be pointed out. The Fourier coefficient $A_{\omega_\ell}^{(i)}$ of Eq. (2.18) may be small either because $\partial c_i / \partial u_\ell$ is small over

the whole range of integration of Eq. (2.19), which is the case discussed above, or because $\partial c_i/\partial u_\ell$ changes sign one or more times in the range of integration. Thus, a small value of $A_{\omega_\ell}^{(i)}$ does not necessarily imply that the concentration c_i is insensitive to changes in the rate coefficients. The remedy for this difficulty would be to find a relation between the Fourier coefficients, or a combination of Fourier coefficients, and an everywhere positive (or everywhere negative) function of the rate of change of the concentrations with rate coefficients, such as for instance $\langle(\partial c_i/\partial u_\ell)^2\rangle$. We have, however, not been able to establish such a relationship and it seems doubtful that a simple relationship of this form exists. In carrying out computer calculations it should, however, not be too difficult to verify whether $\partial c_i/\partial u_\ell$ at any given time t is monotone or not in the range of integration over the $\vec{u}$ space.

Thus while one can assert that a large $A_{\omega_\ell}^{(i)}$ implies high sensitivity of the concentration of species i with respect to changes in the rate coefficient k_ℓ, the converse statement does not necessarily follow without checking on the monotonicity of $\partial c_i/\partial u_\ell$ as discussed above.

III. Choice of the Frequencies ω_i.

As we have mentioned above, the application of Weyl's theorem in going from s space, Eq. (2.6), to the $\vec{u}$ space, Eq. (2.16), via the $\vec{\theta}$ space, Eq. (2.8), must lead to an error in the analysis since we use commensurate (integer) frequencies. This error can be minimized by a judicious choice of the integer frequencies ω_i and the number and magnitude of the m values of the parameter s given by Eq. (2.24). We limit ourselves here to some qualitative remarks which will, however, clearly indicate the nature of the problem.

The integer frequencies ω_i lead, according to Eqs. (2.7) and (2.24), to a covering of the n dimensional $\vec{\theta}$ space by an array of points as q takes on its integer values q=1,2,...,m. Clearly one obtains a better coverage of the $\vec{\theta}$ space and thus reduces the error in applying Weyl's theorem if one can increase the density of points in the n-dimensional hypercube and if one can distribute the points uniformly within the space. Since $\vec{\omega}$ and q are both integer, the points $\vec{\omega} \cdot s$ (mod 2π) will form a regular lattice in $\vec{\theta}$ space. Our objective will be to make this point lattice, which is completely generated by a unit cell, as uniform as possible in all n directions by a judicious choice of the ω's. As our measure of uniformity we take a nypercubic unit cell. Without further information about the behavior of the output function this seems the most reasonable choice.

For a fixed number m of s points, chosen for computational convenience, we will try to find a vector $\vec{\omega}$ (of the infinite set of $\vec{\omega}$'s) which gives rise to a nypercubic unit cell. Once having done this we can assert, without loss of generality, that $\frac{2\pi\vec{\omega}}{m}$ lies along one edge of this hypercubic unit cell whose length is $\frac{2-|\vec{\omega}|}{m}$. There are now two ways to compute the volume V of the

unit cell. In the n dimensional $\vec{\theta}$ space, it follows from the above construction that

$$V = \left(\frac{2\pi|\vec{\omega}|}{m}\right)^n \tag{3.1}$$

But we also know that the total volume of the n-dimensional $\vec{\theta}$ space is $(2\pi)^n$. Since there are m unit cells in that space, it follows that

$$V = \frac{1}{m}(2\pi)^n \tag{3.2}$$

Equating (3.1) and (3.2) then yields

$$|\vec{\omega}| = m^{\frac{n-1}{n}} \tag{3.3}$$

for the relation between the minimum length of the vector $\vec{\omega}$, the dimension n and the number of s points, m, for a point lattice composed of hypercubic unit cells.

The condition expressed in equation (3.3) yields important insight into the judicious choice of the frequencies ω_i. For systems with large dimensions, i.e. a large number n of rate coefficients (or coupling parameters in general), $|\vec{\omega}|$ approaches m. Thus, the choice of the number m of s points for the numerical computation determines the value of $\vec{\omega}$ and thus guides one in the choice of the ω_i's. Since one would expect the error in the analysis due to the use of integer frequencies ω_i to be of order 1/m, i.e. inversely proportional to the number of unit cells, it is evident that one should choose a large value of m to carry out the calculations. This in turn implies from Eq. (3.3) a large $|\vec{\omega}|$.

The analysis leading to Eq. (3.3) is based on the construction of unit cells which are <u>exact</u> hypercubes. Since $|\vec{\omega}|$, m and n are all integers it may

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not be possible to fulfill condition (3.3) exactly for all (arbitrary) choices of m and n. It is easy to show this. Let us, for instance, square both sides of Eq. (3.3) and let n = 5. We are then required to find an integer m such that we can express a sum of n squares, $|\vec{\omega}|^2$, as $m^{8/5}$. Clearly, this is possible, if at all, only for certain special values of m. To be more realistic, we should weaken our criteria for uniformity of the point lattice by stipulating unit cells which are as close as possible to hypercubic and then rewrite Eq. (3.3) as

$$|\vec{\omega}| \simeq m^{\frac{n-1}{n}} \qquad\qquad (3.4)$$

For $n \gg 1$, for which both (3.3) and (3.4) reduce to $|\vec{\omega}| \simeq m$, it should be possible to obtain a more nearly exact hypercubic unit cell.

The question as to the "optimum" choice of the ω's has been considered by a number of authors, using a different approach from that presented above, in connection with the general problem of the approximate evaluation of multi-dimensional integrals via discrete summations[4]. Korobov's book has tables of ω_i's for a given number of points m (for m prime) and dimension n up to n = 10. These tables are reprinted in the book by A. H. Stroud. It is inter-esting and comforting to note that although these tables were computed from completely different criteria than those employed by us, the Korobov $\vec{\omega}$'s indeed generate hypercubic unit cells to a very good approximation for all his sets of $\vec{\omega}$ for which we have carried out the appropriate calculations.

Korobov's analysis of the error in the use of integer frequencies yields explicit prescriptions for calculating the "optimum" set of ω_i's as given in his tables. Our approach presented above does not yield such an explicit algorithm. We plan to develop such an algorithm and then compare our sets of $\vec{\omega}$ with those of Korobov in a subsequent publication.

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As stated above, if one wishes to decrease the error in the integer ^frequency^ analysis, one should use a large number   m of s points and thus a large $|\vec{\omega}|$. It can readily be verified from Eq. (2.6) that for large ω_i one needs to evaluate $c(s)$ for a larger number of s values in order to obtain an accurate value for the Fourier coefficient $A^{(i)}_{\omega_\ell}$. This requires more extensive computer calculations. A reasonable compromise between these two effects needs to be adopted.

The transformation from $\vec{u}$ space to $\vec{\theta}$ space as given by Eqs. (2.3) and (2.7) will also effect the error term since the specific transformation which is chosen determines the rate of change of the function $c(s)$ as a function of s. We are faced here with an interesting problem in compensating effects. Either the transformation $u_i = u_i(\theta)$ is singular or the weight function $p(u_i;a_i)$ is singular at one or more values of u_i. For the chosen transform it is readily verified from Eqs. (2.15) and (2.20) that u_i diverges at $\theta = \pi/2$ and $\theta = 3\pi/2$, but at these points $p(u_i;a_i) = 0$. This same effect will be found for any transformation and its associated weight function. Thus in the regions of $\vec{\theta}$ space where the transformation is divergent the associated weight function will always compensate. We are therefore led to expect that the choice of the transformation function will not significantly effect the final numerical results. This is born out by the data presented in paper II.

Acknowledgements

REFERENCES

I. THEORY

1. See e.g., G. Gavalas, "Non-linear Differental Equations of Chemically Reacting Systems," Springer Verlag, N.Y., (1968); D. Bedeaux, C.N. Fortuin, and K.E. Shuler, to be published.

2. See e.g., V.I. Arnold and A. Arey, "Ergodic Problems of Classical Mechanics, Benjamin, N.Y. (1968).

3. H. Weyl, Am. J. Math, 60, 889 (1938).

4. See e.g., N.M. Korobov, Number-Theoretic Methods in Approximate Analysis, Moscow (1963); S. Haber, SIAM Review, 12 , 481 (1970); A.H. Stroud, Approximate Calculation of Multiple Integrals, Prentice Hall, Inc., N.Y. (1972); S.K. Zaremba (Ed.), Application of Number Theory to Numerical Analysis, Acad. Press, N.Y. (1972) pp.39 and 121.

A STUDY OF THE SENSITIVITY OF COUPLED

REACTION SYSTEMS TO UNCERTAINTIES

IN RATE COEFFICIENTS

II. APPLICATIONS[‡]

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ABSTRACT

The Fourier amplitude method developed in Part I as a diagnostic tool for determining the sensitivity of the results of complex calculations to the parameters which enter these calculations has been applied to two chemical reaction systems involving sets of coupled, non linear rate equations. These were: a) a 5 reaction set describing the high temperature (6000°K) dissociation of air and b) a 9 reaction set describing the constant temperature (2000°K) combustion of H_2 and O_2. We have evaluated the Fourier amplitudes for all the species at a number of different times for both reaction systems. The analysis of these results verifies the claims made in part I. The relative magnitudes of the Fourier amplitudes showed a several order of magnitude distribution which permitted a clear distinction of the relative sensitivity of the species concentration to uncertainties in the rate coefficients. The conclusions based on the Fourier amplitude method for these two reaction systems are in excellent agreement with sensitivity predictions which could be made on the basis of previous kinetic studies of these systems.

I. INTRODUCTION

In the preceding paper, hereafter referred to as I,[1] we developed a diagnostic technique to investigate the sensitivity of the solution of large sets of coupled, non-linear equations to uncertainties or changes in the coupling parameters. For brevity, we will refer to this method as FAST, the Fourier Amplitude Sensitivity Test. In this paper we wish to demonstrate the utility of FAST by applying it to a study of the sensitivity of two sets of coupled non-linear rate equations describing, respectively, the high temperature dissociation of air and the high temperature $H_2 - O_2$ reaction. The specific objective of the calculations described here was to determine the sensitivity of the various species concentrations at a particular time to assumed uncertainties in the rate coefficients which enter into these calculations.

In Section II we summarize the steps which must be carried out in the application of FAST to any system of coupled non-linear equations and discuss the choice of frequencies and the number of sampling points to be used. In Section III, we present the sensitivity analysis for the two chemical reaction systems. Section IV contains some concluding remarks.

II. GENERAL REMARKS ON APPLICATION OF FAST

We wish to determine the sensitivity of an "output function", in our case the calculated concentration of a particular species at a particular time, to assumed uncertainties in the rate coefficients entering the rate equations. We write this output function as

$$c(k_1, k_2, \ldots, k_n) \equiv c(\vec{k}) \tag{2.1}$$

where $\vec{k}$ is the n-component vector of the rate coefficients $k_1, k_2, \ldots, k_n$.

The application of FAST is carried out via the following steps:

Step 1) One must choose a set of n integer frequencies, $\{\omega_1, \omega_2, \ldots, \omega_n\}$, where n is the number of independent rate coefficients which determine the value of the output function.

Step 2) One frequency of this set is now assigned arbitrarily to each rate coefficient by (see I.2.2):

$$k_i = k_i^{(o)} e^{u_i} \qquad (2.2)$$

$$u_i = u_i^{(o)} \sin \omega_i s \qquad (2.3)$$

where $k_i^{(o)}$ is the best estimate of the rate coefficient, s is a parameter and the $u_i^{(o)}$ are the endpoints of the estimated ranges of uncertainties of the rate coefficients k_i. If a rate coefficient is known precisely, i.e. with zero uncertainty, then $k_i = k_i^{(o)}$ which implies $u_i^{(o)} = 0$. The endpoints $u_i^{(o)}$ are specified as part of the input data and their values should be based on the best judgement of the investigator.

Step 3) The output function $c(\vec{k}) = c[\vec{k}(s)]$ is now Fourier analyzed in s to obtain the sine amplitudes A_{ω_i} corresponding to the input frequencies ω_i. This analysis requires the evaluation of $c[\vec{k}(s)]$ for N values of s, where N is an integer which depends on the frequency spectrum of $c[\vec{k}(s)]$.

These steps will now be discussed in more detail.

a) Choice of Frequencies ω_i

In section III of part I we have presented a discussion of the choice of the set of frequencies $\{\vec{\omega}\}$ and have also given there a set of references (ref. 4) which contain both discussions of optimal choices of sets of frequencies

as well as tables of frequencies which could be used for FAST. For the calculations presented here we have developed our own set of frequencies. We have done so to obtain a better insight in how to handle the calculations involved in the Fourier analysis method. In a follow-on study we plan to investigate whether our method of choosing frequencies yields better, equivalent or worse sets for use in FAST than those presented in reference 4 of part I.

Since we will carry out computer calculations, we are limited to rational (or, equivalently, integer) frequencies. For the coupled non-linear equations under study here, this means that in addition to the input frequencies ω_i and their multiples, various linear combinations of integer multiples of ω_i ("interference frequencies") will appear in the spectrum of $c[\hat{k}(s)]$. This presents a problem in our analysis since the Fourier sine amplitude of frequency ω_ℓ is to reflect only the effect of the uncertainty in the value of the rate coefficient k_ℓ. Clearly, if an interference frequency coincides with one of the input frequencies ω_i, say ω_ℓ, the corresponding Fourier amplitude A_{ω_ℓ} will not only reflect changes in k_ℓ but also in other rate coefficients. Thus, for example, if $\omega_1 + \omega_3 - \omega_4 = \omega_2$, the amplitude A_{ω_2} is identical with $A_{(\omega_1 + \omega_3 - \omega_4)}$ and will therefore reflect not only changes in k_2, but also in k_1, k_3 and k_4.

One therefore needs to choose a linearly independent set of input frequencies ω_i such that

$$\sum_{i=1}^{n} a_i \omega_i \neq 0 \; ; \qquad\qquad a_i \text{ integer} \qquad\qquad (2.4)$$

for

$$\sum_{i=1}^{n} |a_i| \leq M + 1 \qquad\qquad (2.5)$$

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where M is a parameter at the disposition of the investigator. We refer to such a set as being free of interferences to order M. The larger the chosen value of M, the greater the likelihood that the Fourier amplitude of each input frequency reflects solely the uncertainty of the corresponding rate coefficient. On the other hand, as discussed in section III of part I and below, the larger the chosen value of M, the larger the maximum value, ω_{max}, of the input frequencies ω_i which will still satisfy (2.4) and (2.5) and, correspondingly, the larger the set N of points s which will be required for the evaluation of the Fourier amplitudes. For the calculations presented in this paper we have chosen M = 4. In Table I we present sets of frequencies which are free of interferences to 4th order for systems with dimensionality n from 5 to 19, i.e. for systems with from 5 to 19 independent rate coefficients. These frequencies were determined via computer by a trial and error procedure. The sets of frequencies listed here have the smallest value of ω_{max} satisfying conditions (2.4) and (2.5) and are referred to as "minimal sets".

b) <u>Assignment of Frequencies to Rate Coefficients</u>

The frequencies $\{\omega_1, \omega_2, \ldots, \omega_n\}$ are assigned to the rate coefficients $\{k_1, k_2, \ldots, k_n\}$ arbitrarily since the results of these calculations, in order to be useful, must be independent of both the frequency set and the assignment of the frequencies. To check that the spectrum of the output function does not contain interfering frequencies which coincide with the input frequencies, and thus affect the results, one should reassign the frequencies to the various rate coefficients and repeat the Fourier analysis. If the calculated Fourier amplitudes are invariant in magnitude and sign to these permutations, then the set of frequencies is free of interferences to the order of the dimensionality of the set of rate equations and the results of these calculations are reliable. If,

on the other hand, some of the Fourier amplitudes vary greatly with the permutations of the frequency assignments, a better set of input frequencies must be generated. By "better" we refer to a set $\{\omega\}$ with a larger parameter M and a higher ω_{max}. We have carried out such a permutation analysis for the $N_2 - O_2$ system discussed below and verified that our sets of input frequencies yielded Fourier amplitudes $A_{\omega_\ell}^{(i)}$ which were invariant to the frequency permutations.

c) Calculation of Fourier Amplitudes

As discussed in section II of part I, we are only interested in the Fourier sine amplitudes. For an input frequency ω_ℓ, the amplitude is

$$A_{\omega_\ell} = \frac{1}{2\pi} \int_0^{2\pi} c[\vec{k}(s)] \sin \omega_\ell s \, ds \qquad . \tag{2.6}$$

To compute this integral, one must evaluate the function $c[\vec{k}(s)]$ at a set of points in the interval $0 \leq s \leq 2\pi$. In the absence of any information on the form of the output function c we take the points to be equally spaced in that interval,

$$s = \frac{2\pi q}{N} \quad , \quad q = 1, 2, \ldots, N \tag{2.7}$$

where N is some integer. With these equally spaced points we can now conveniently relate the Fourier coefficient A_{ω_ℓ} as defined by the integral (2.6) to the sum

$$A^*_{\omega_\ell} = \frac{2}{N} \sum_{q=1}^{N} \sin \omega_\ell s_q \, c[\vec{k}(s_q)] \tag{2.8}$$

where

$$A^*_{\omega_\ell} = A_{\omega_\ell} + \epsilon_{\omega_\ell} \qquad . \tag{2.9}$$

The error term ϵ_{ω_ℓ} is given by

$$\epsilon_{\omega_\ell} = \sum_{m=1}^{m} \sum_{j} A(mN - \omega_j) \tag{2.10}$$

where ω_j is any frequency in the spectrum of $f[\bar{k}(s)]$ which satisfies

$$mN - \omega_j = \omega_\ell \tag{2.11}$$

This error term is due to "aliasing" which inevitably occurs whenever a finite number of points are chosen on an interval to evaluate Fourier amplitudes. For example, if N equally spaced points are used, the amplitudes $A_{\omega_\ell}^{(i)}$ for ω_ℓ will unavoidably include the amplitudes of a component of frequency ω_j present in c(s) which satisfies the relation $\omega_\ell = mN - \omega_j$ where m is an arbitrary integer. The value of N is chosen to be the smallest integer such that

$$\sum_{i=1}^{n} b_i \omega_i \neq mN \quad , \quad b_i, m \text{ integers} \tag{2.12}$$

for

$$\sum_{i=1}^{n} |b_i| \leq M + 1 \tag{2.13}$$

The Fourier amplitudes A_{ω_ℓ} have been evaluated using Eqs. (2.8) through (2.10).

If the output function c(k) could be expressed as a polynomial of degree less than or equal to M in the variables u_i, i = 1, ..., n, where (see Eq. 2.2)

$$u_j = \ln \; (k_j/k_j^{(o)}) \tag{2.14}$$

then the conditions (2.12) and (2.13) imply that $\epsilon_{\omega_\ell} = 0$ so that

$$A_{\omega_\ell}^* = A_{\omega_\ell} \tag{2.15}$$

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The conditions (2.11) through (2.13) also determine N the minimum number of s points required for the evaluation of $c[\bar{k}(s)]$. These are listed in Table I.

The Fourier amplitudes are related to a multiple integral of an output function over the uncertainty space (see I. 2.12). One way of obtaining the Fourier amplitudes without the troublesome interferences and aliasing involved in the method discussed above would be to evaluate the n-dimensional integral of Eq. (I. 2.12) directly. We have done this $\underline{via}$ simple Monte Carlo integrations. Our results show that the number of integration points required by the Monte Carlo method to give a comparable accuracy is much greater than the number required in the Fourier analysis. Stated another way, for a given number of integration points (we used 200), the degree of accuracy of the Fourier method detailed above far surpasses that of the Monte Carlo integration.

d) Choice of the Weight Function

As emphasized in I, our final result, i.e. the relation

$$A_{\omega_\ell}^{(i)} \propto \langle \partial c_i / \partial u_\ell \rangle \tag{2.16}$$

involves a weight function $p(u_i)$ which can be interpreted as a distribution function in u space which weights the uncertainty in the rate coefficients. In our treatment in part I, we used the weight function (see Eq. 2.20)

$$p(u_i) = \frac{a_i}{\cosh a_i u_i} \tag{2.17}$$

which had several desirable properties. It is, for instance, bell shaped about $u_i = 0$ corresponding to $k_i = k_i^{(o)}$, the "best" value of the rate coefficient k_i. For computational convenience, we have used two different weight functions for the calculations presented in section III below corresponding to two different

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transformations $u_i = u(\omega_i s)$. As we had hoped and expected, our results did not depend significantly on the choice of the weight function. This indicates that our output functions $c(k)$ were "well behaved", i.e. did not have any large local excursions in $\ddot{u}$ space. It is also in agreement with the discussion in the last paragraph of section III of part I.

As is shown in part I, the form of the weight function $p(u_i)$ depends upon the choice of the transformation function f of Eq. (I.2.3). For the Fourier amplitude method to be at all useful, our results on the relative magnitudes of the Fourier amplitudes must clearly be independent of the explicit form of the transformation function. The insensitivity of our results to our choice of transformation function (and thus of the weight functions) verifies the validity of FAST in this respect.
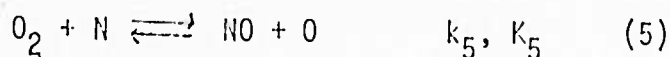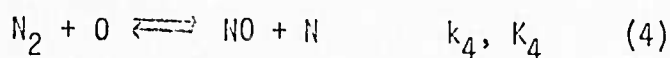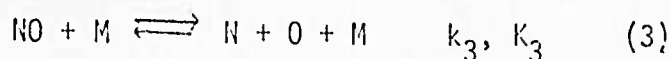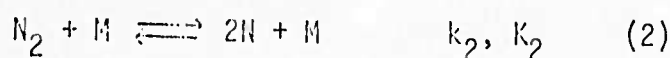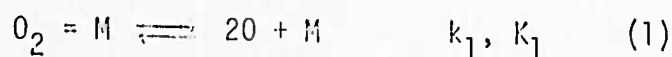
III. APPLICATION OF FAST TO CHEMICAL SYSTEMS

We have applied FAST to two relatively simple reaction systems as a test of its utility as a diagnostic tool. Both systems were assumed, for simplicity, to react at constant temperatures and volume. These restrictions are in no way necessary for the application of FAST. The concentrations were

integrated in time with a code using Gear's[2] algorithm. These integrations were carried out once for each of the N values of s with the corresponding values of the n rate coefficients, $\tilde{k}(s)$, up to some time t. This yielded the output function $c_i[\tilde{k}(s),t]$, i.e. the concentration of species i, i=1, 2, ..., m, as a function of time. The Fourier analysis of $c_i[\tilde{k}(s),t]$ was then carried out at several selected times. The uncertainties in the rate coefficients were arbitrarily assumed to be much larger than warranted by the available experimental data in order to check out FAST. It should therefore be pointed out again that the primary purpose of the calculations presented here is to demonstrate the validity and utility of FAST as a diagnostic tool and not to provide new information about the selected reaction systems.

a) High Temperature Air Reaction

We consider the following simplified reaction system[3]

$$O_2 + M \rightleftharpoons 2O + M \qquad k_1, K_1 \qquad (1)$$

$$N_2 + M \rightleftharpoons 2N + M \qquad k_2, K_2 \qquad (2)$$

$$NO + M \rightleftharpoons N + O + M \qquad k_3, K_3 \qquad (3)$$

$$N_2 + O \rightleftharpoons NO + N \qquad k_4, K_4 \qquad (4)$$

$$O_2 + N \rightleftharpoons NO + O \qquad k_5, K_5 \qquad (5)$$

The rate coefficients k_i, i=1, ..., 5, refer to the forward reactions, the rate coefficients k_{-i} for the reverse reactions are obtained from the equilibrium constant K_i through the relation $K_i = k_i/k_{-i}$. In the system and the one discussed below in IIIb, the equilibrium constants are assumed to be known exactly, i.e. with zero uncertainty. The forward and reverse rate coefficients k_i, k_{-i} for each reaction therefore have identical uncertainties and the number of

independent uncertainties is equal to the number of equilibrium constants. It is, of course, not necessary to proceed this way and one can instead assign different uncertainties to the forward and reverse rate coefficients which reflect uncertainties in the equilibrium constants.

The system was assumed to react at a constant temperature of 6000°K and constant volume. The rate coefficients, equilibrium constants and initial conditions used in this calculation are shown in Table II.
The equilibrium constants represent the latest and "best" literature values we could find and the rate coefficients listed in this table are the $k_i^{(o)}$ of Eq. (2.2). In Fig. 1 we show a plot of the time evolution of this reaction system obtained from the integration of the rate equations using the rate coefficients $k_i^{(o)}$ of Table II.

While the real uncertainty of these rate coefficients is not too large, we assumed arbitrarily for the purpose of testing FAST that the experimental uncertainties were $\pm$ two orders of magnitude for each of the five independent sets of rate coefficients. To take account of this uncertainty we then write (see Eq. (2.2))

$$k_i^{(o)} e^{-4.606} \leq k_i \leq k_i^{(o)} e^{4.606} \quad ; \quad i = 1, \ldots, 5 \quad . \tag{3.1}$$

For our sensitivity analysis we used the frequency set (see Table I)

$$\{\omega\} = (2, 42, 62, 74, 90) \tag{3.2}$$

for which the smallest number N of evenly spaced points satisfying the conditions of Eqs. (2.4, 2.5, 2.12, 2.13) in the s interval, $0 \leq s \leq 2\pi$, is 191.

We carried out the Fourier analysis of the output function $c_i[\vec{k}(s)]$ at $t = 10^{-6}$ sec and 10^{-4} sec. From Eqs. (2.2), (2.3) and (3.1) we have

$$u_i = 4.606 \sin \omega_i s \tag{3.3}$$

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The concentrations of the various species, N_2, O_2, NO, O, N, were calculated at 10^{-6} sec and 10^{-4} sec for each of the 191 s values by integrating the rate equations. The 191 values of the concentration of the above species at a given time define the output function $c_i[\bar{k}(s)]$ which is now Fourier analysed by computing the Fourier coefficients from Eqs. (2.8) through (2.13) using the set of input frequencies of Eq. (3.2). An example of the function $c_i[\bar{k}(s)]$ for NO at $t = 10^{-4}$ sec is shown in Fig. 2. This curve has been drawn by connecting the 191 calculated concentrations of NO (one for each of the 191 evenly spaced values of s) by straight lines.

The results of the Fourier analysis at $t = 10^{-6}$ sec are shown in Table III. The high values of the Fourier amplitudes associated with the rate coefficients k_1, k_{-1} for the concentration of O and O_2 (see blocks 1 and 2 of Table III) indicate that a variation in k_1 and k_{-1} has a greater effect on the concentration of O and O_2 than the variation of any of the other rate coefficients. This follows immediately from Eq. (2.16), where now i refers to the O atoms and O_2 molecules and $\omega_\ell = 2$ refers to the rate coefficients k_1 and k_{-1}. We can rephrase this by saying that, at this early time in the reaction, only reaction (1) is important in the production of O atoms and the disappearance of O_2 molecules. The sign of the amplitudes in the last column can be understood from Eq. (2.16) according to which the amplitude $A_{\omega_\ell}^{(i)}$ is proportional to $(\partial c_i/\partial u_\ell)$. Thus the negative sign of the Fourier amplitude for k_1 for the concentration of O_2 (block 1, Table III) simply indicates that $[O_2]$ decreases with increasing k_1. The positive sign for the Fourier amplitude for k_1 for the concentration of O atoms (block 2, Table III) indicates that [O] increases with increasing k_1. From the relative magnitudes of the Fourier amplitudes in blocks 4 and 5 of Table III, it will be noted that the formation of N and NO at these early times
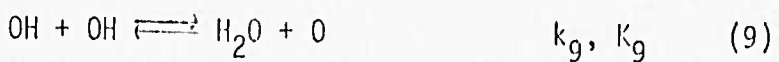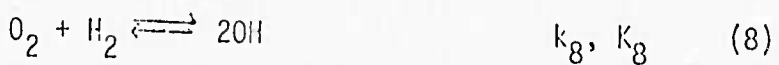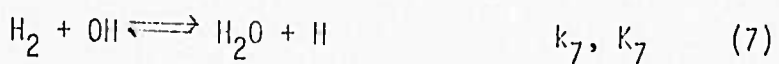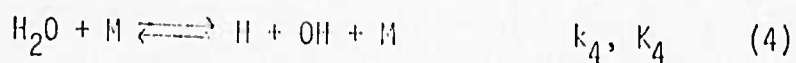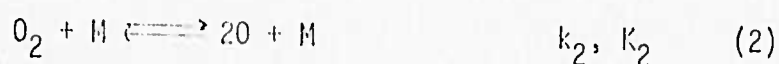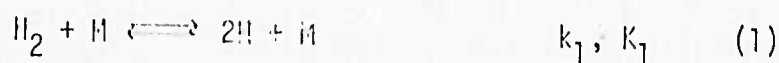
in the reaction is most sensitive to reactions (1) and (4). This is quite reasonable since at $t = 10^{-6}$ sec the formation of N and NO via reactions (2) and (5) cannot play any important role owing to the small value of $k_2^{(o)}$ as compared to $k_1^{(o)}$ (see Table II). A number of other conclusions as to the sensitivity of the concentrations of the various species with respect to variation of the rate coefficients can be drawn from a study of the results in Table III. All these conclusions are in accord with one's knowledge and intuition of this rather simple reaction system.

In Table IV we present our results for $t = 10^{-4}$ sec. At this time, as can be seen from Fig. 1, the concentrations of reactants and products are, except for N_2, significantly different from their initial values. The coupling between the various reactions has come into play much more strongly at this later time and one would expect that the influence of the uncertainties in the rate coefficients on the concentrations of the various species is more complex. This can readily be verified from the data in Table IV, where there is now no longer such a pronounced order of magnitude effect in the Fourier amplitudes. Let us arbitrarily use a factor of about 10 to distinguish between the "relatively important" amplitudes (i.e. the concentration of the species is very sensitive to the change of a specific rate coefficient) and the "relatively unimportant" amplitudes (i.e. the concentration of the species is not very sensitive to the change of a specific rate coefficient). Then the data of Table IV indicates that $[O_2]$ and $[O]$ are affected primarily by uncertainties in k_1, $[N_2]$ is affected about equally by uncertainties in all of the rate coefficients, $[N]$ is most affected by uncertainty in k_1, and $[NO]$ is least affected by uncertainty in k_2. The least "sensitive" rate coefficient is k_2, which determines the rate

of dissociation of N_2. This is not surprising since $k_2^{(o)}$ is smaller than the other rate coefficients by 2 to 4 orders of magnitude. The important point to note is that owing to the strong coupling of all the reactions at this stage of the kinetic development, a number of the elementary rate processes contribute significantly to the production and removal of most of the species, so that the concentration of these species are quite sensitive to uncertainties in <u>several</u> rather than just <u>one</u> rate coefficient. This result is certainly not unexpected.

b) The H_2 - O_2 Reaction

The H_2 - O_2 combustion system was modeled by the following set of chemical reactions[4]:

$$H_2 + M \rightleftharpoons 2H + M \qquad k_1, K_1 \qquad (1)$$

$$O_2 + M \rightleftharpoons 2O + M \qquad k_2, K_2 \qquad (2)$$

$$OH + M \rightleftharpoons O + H + M \qquad k_3, K_3 \qquad (3)$$

$$H_2O + M \rightleftharpoons H + OH + M \qquad k_4, K_4 \qquad (4)$$

$$H + O_2 \rightleftharpoons OH + O \qquad k_5, K_5 \qquad (5)$$

$$O + H_2 \rightleftharpoons OH + H \qquad k_6, K_6 \qquad (6)$$

$$H_2 + OH \rightleftharpoons H_2O + H \qquad k_7, K_7 \qquad (7)$$

$$O_2 + H_2 \rightleftharpoons 2OH \qquad k_8, K_8 \qquad (8)$$

$$OH + OH \rightleftharpoons H_2O + O \qquad k_9, K_9 \qquad (9)$$

The system was assumed to react at a constant temperature of 2000°K and constant volume, with only H_2 and O_2 present at t = 0.

The initial conditions, rate coefficients and equilibrium constants are shown in Table V. The rate coefficients listed in this table are the $k_i^{(o)}$ of Eq. (2.2); the equilibrium constants are assumed to be known with zero uncertainty.

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We assumed arbitrarily that the experimental uncertainties for each of the nine independent rate coefficients were ± one order of magnitude so that

$$k_i^{(o)} e^{-2.303} \leq k_i \leq k_i^{(o)} e^{2.303} \quad ; \quad i = 1, 2, \ldots, 9 \quad . \quad (3.4)$$

For our analysis we used the frequency set

$$\{\omega\} = (19, 59, 91, 113, 133, 143, 149, 157, 161) \quad (3.5)$$

for which the smallest number N of evenly spaced points in the s interval, $0 \leq s \leq 2\tau$, is 630.

A plot of the concentrations of the various species for the time interval $10^{-4} \leq t \leq 10$ seconds, calculated with the $k_i^{(o)}$ of Table V is shown in Fig. 3. We have employed FAST to study the sensitivity of the species concentrations to uncertainties in the rate coefficients at 10^{-8} seconds and 10^{-3} seconds. These results are shown in Tables VI and VII.

At the very early time of 10^{-8} seconds (Table VI), the H_2 and O_2 concentrations have not changed significantly from their original value (to within 8 significant places) and the Fourier amplitudes are merely round-off error. For H atoms, reaction (1) seems to be the major contributor to its formation at this early time and its rate coefficient is the most sensitive in determining the accuracy of [H]. Reactions (7) and (8), which together also produce H atoms, are also important but the concentration of H atoms is not as sensitive to k_7 and k_8 as it is to k_1. The sensitivity of [H] to these two rate coefficients has identical values which is not surprising since [H] is proportional to $k_7 \cdot k_8$ at this early time. The same argument also holds for the production of H_2O since its concentration at 10^{-8} seconds is proportional to $k_7 \cdot k_8$. The H_2O concentration

is also sensitive to k_5, since reaction (5) appears to be partly responsible for the production of the OH which enters into reaction (7). The concentration of O atoms is most sensitive to k_2 which is again as expected. Finally, the OH concentration is most sensitive to k_8 which is also most reasonable, since at this early time, only the direct reaction between O_2 and H_2 would be expected to effect the OH concentration. Again, the results of FAST are in good agreement with what could be predicted on the basis of chemical knowledge.

At $t = 10^{-3}$ seconds (Table VII) the story is quite different. As can be seen from Fig. 3, significant changes from the initial concentrations have occured by this time, and the reactions are now strongly coupled. This is reflected in the array of Fourier amplitude in Table VII as compared to those of Table VI. Now, for instance, rate coefficient k_5 corresponding to the chain branching step (5) which produces H and O atoms is the most influential one in controlling the concentration of all species. The H atoms concentration, in addition, is equally sensitive to k_7. All other rate coefficients, except for k_3, which is very small for all species, have about equal sensitivities to within a factor of 10 as measured by their Fourier amplitudes. According to our theory and calculations then, the rate coefficient which needs to be determined with the highest accuracy for the accurate calculation of all species concentration at 10^{-3} seconds is k_5 with k_7 next in line. Uncertainties in the other rate coefficients will have a smaller effect on the species concentrations.

IV. CONCLUDING REMARKS

It should be realized that the applications presented here are only a first cut at the subject. It appears that FAST is a useful diagnostic tool in determining the sensitivity of the results of complex calculations to the parameters which enter the calculations. The Fourier amplitude method clearly needs further testing on more complicated systems than the ones dealt with in this paper. Such tests should also involve comparison with various types of "brute force" calculations.

In addition to applications to larger systems, there are also a number of theoretical-computational questions which need further investigation. Some examples are: the influence of the range of uncertainties, with different uncertainties for different coupling parameters, on the relative magnitudes of the Fourier amplitudes; the influence of the choice of the input frequencies $\{\omega\}$ and the spacing of the N values of the parameter s on the Fourier amplitudes; and the question whether the absolute magnitude of the Fourier amplitudes can be used as a predictor for the actual change of the output function for a given change of the coupling parameter. Additional work is being carried out to answer these questions.

V. ACKNOWLEDGEMENT

REFERENCES

1) R. I. Cukier, C. M. Fortuin, K. E. Shuler, A. G. Petschek and J. H. Schaibly,
    J. Chem. Phys. ... (preceding paper)

2) C. W. Gear, The Numerical Integration of Stiff Differential Equations,
    University of Illinois, Dept. of Computer Sciences Report No. 221,
    Jan. 1967.

3) The equilibrium constants were calculated from data in B. J. McBride,
    Thermodynamic Properties to 6000°K for 210 Substances Involving the
    First 18 Elements, NASA, SP-3001 (1963). The rate coefficients were
    taken from: J. C. Schexnayder and J. S. Evans, NASA Technical Report
    R-108, 1961; H. S. Glick, J. J. Klein, and W. Squire, J. Chem. Phys. $\underline{27}$,
    850 (1957); G. B. Kistiakowski and G. G. Volpi, J. Chem. Phys. $\underline{27}$, 1141 (1957).
    We are aware that more recent "nominal" values of the various rate coefficients
    exist in the literature but feel that the values used in our calculations are
    adequate for the purpose of this paper.

4) The equilibrium constants were calculated from the data in Mc Bride
    (see ref. 2); the rate coefficients were obtained from the compilation of
    G. S. Bahn, Reaction Rate Compilation for the H - O - N System, Gordon and
    Breach Science Publishers, New York (1968).

FIGURE CAPTIONS

Fig. 1.   Time evolution of the H_2 - O_2 system based on the kinetic data in Table II.

Fig. 2.   The function $c_i[\hat{R}(s)]$ for NO at 10^{-4} sec between 0 and 2π as a function of s. This curve has been drawn by connecting the 191 calculated values of the concentrations of NO (corresponding to the 191 values of s) by straight lines.

Fig. 3.   Time evolution of the H_2 - O_2 systems between $t = 10^{-4}$ sec to $t = 10$ sec based on the kinetic data in Table V.
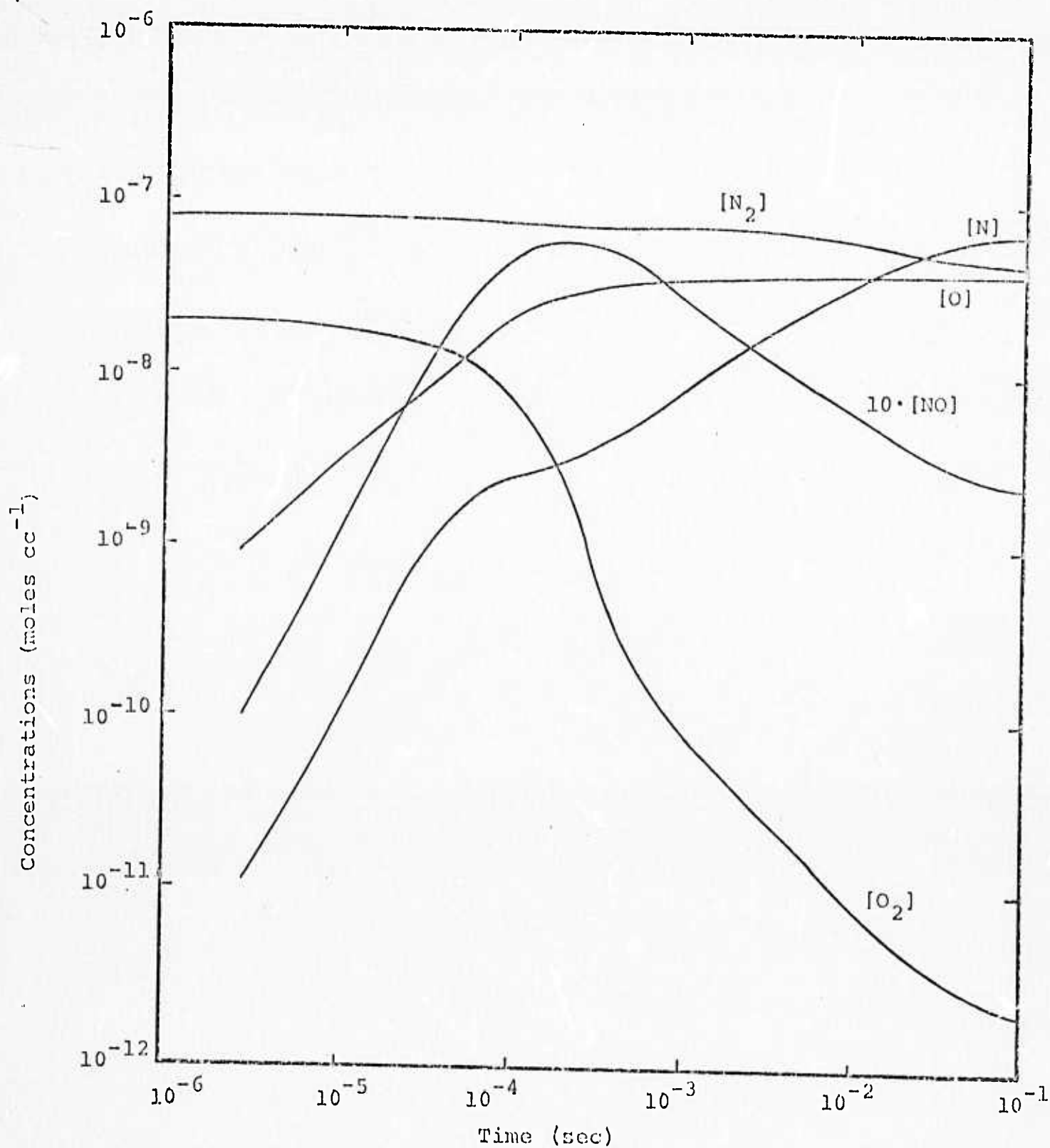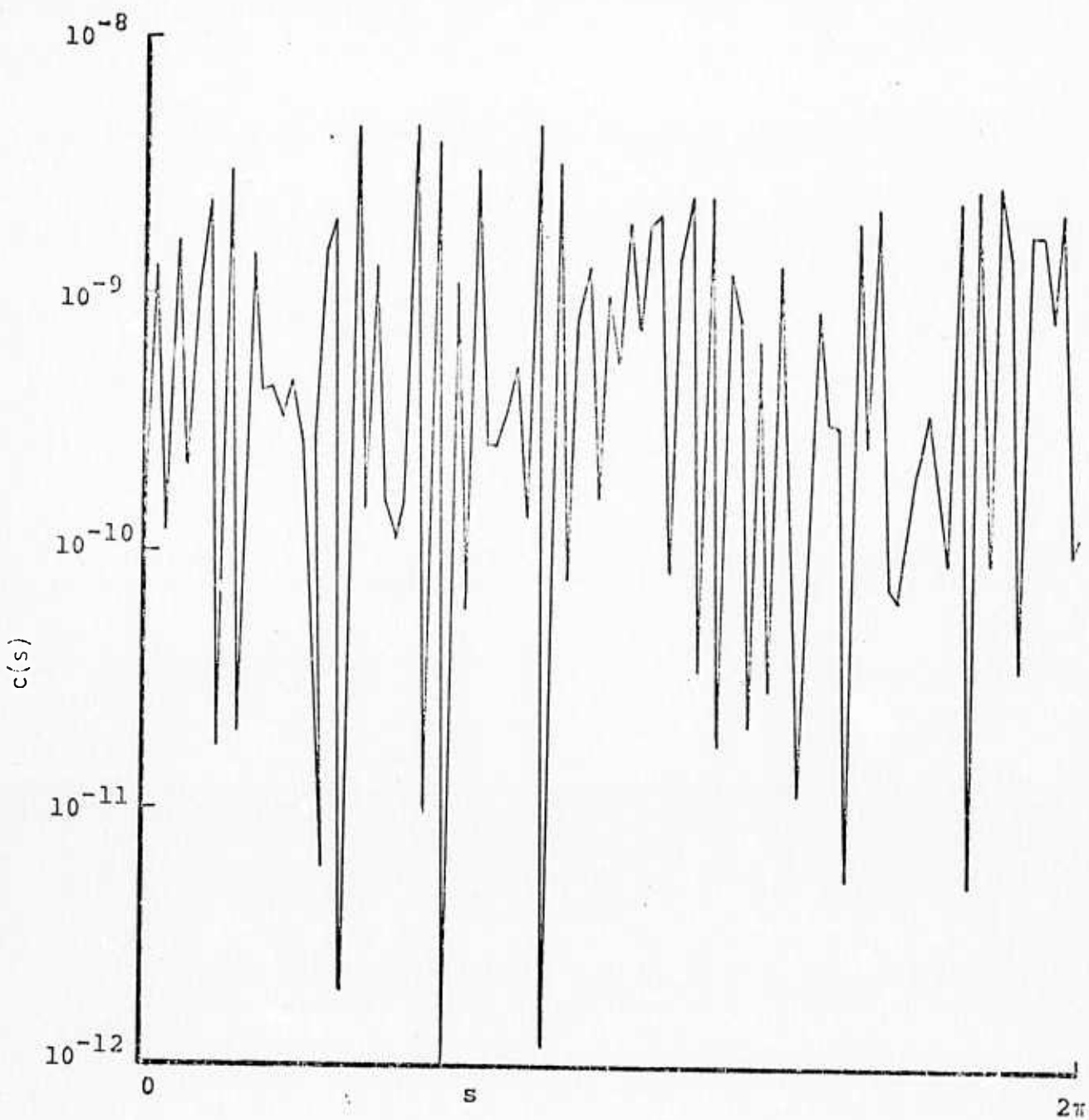
Fig. 1, Schadly + Sluder

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Fig. 2, Schachly + Shuler

20-1-a

Fig. 3, Schatky + Shuler

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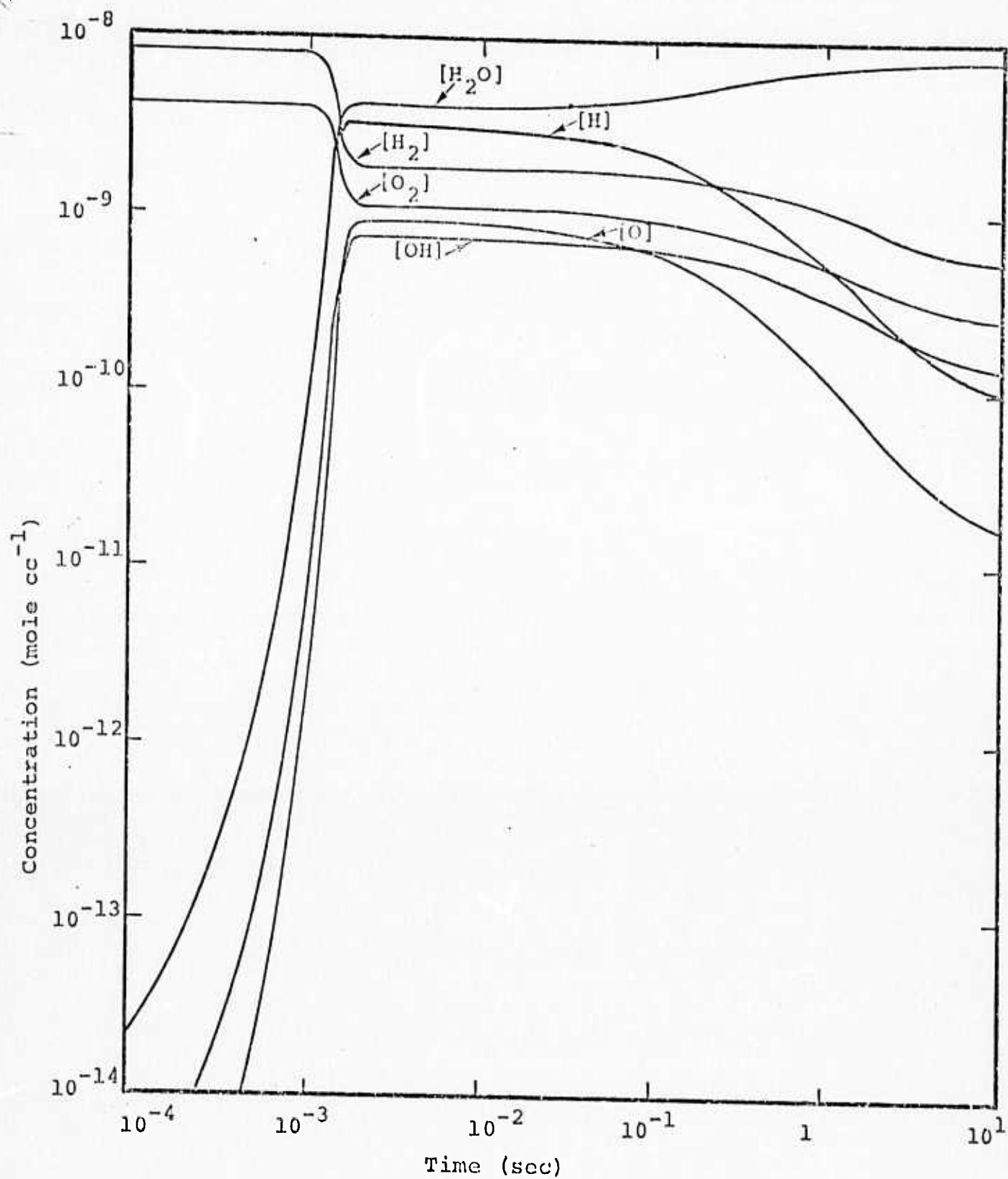
Table I

FREQUENCY SETS AND CORRESPONDING NUMBER OF POINTS AVOIDING INTERFERENCES THROUGH <u>4th</u> ORDER

Dimension (n)	Frequency Set {ω}	Minimum Number of Points (N)
5	11, 21, 27, 35, 39	142
5*	2, 42, 62, 74, 90	191
6	1, 21, 31, 37, 45, 49	182
6*	2, 42, 62, 74, 90, 98	231
7	17, 39, 59, 69, 75, 83, 87	334
8	23, 55, 77, 97, 107, 113, 121, 125	486
9	19, 59, 91, 113, 133, 143 149, 157, 161	630
10	25, 63, 103, 135, 157, 177, 187, 193, 201, 205	806
11	41, 67, 105, 145, 177, 199, 219, 229, 235, 243, 247	974
12	31, 87, 113, 151, 191, 223, 245, 265, 275, 281, 289, 293	1158
13	23, 85, 141, 167, 205, 245 277, 299, 319, 329, 335, 343, 347	1374
14	87, 133, 195, 251, 277, 315, 355, 387, 409, 429, 439, 445, 453, 457	1814

Table II

INITIAL CONDITIONS, RATE COEFFICIENTS AND EQUILIBRIUM CONSTANTS FOR THE HIGH TEMPERATURE AIR REACTION

Initial Conditions

$[N_2] = 8 \times 10^{-8}$ moles/cc

$[O_2] = 2 \times 10^{-8}$ "

Rate Coefficients

$k_1^{(o)} = 8.5 \times 10^{10}$ (moles/cc)$^{-1}$ sec^{-1}

$k_2^{(o)} = 3.0 \times 10^{7}$ "

$k_3^{(o)} = 8.0 \times 10^{9}$ "

$k_4^{(o)} = 9.0 \times 10^{10}$ "

$k_5^{(o)} = 8.0 \times 10^{11}$ "

Equilibrium Constants

$K_1 = 7.8 \times 10^{-4}$ (moles/cc)

$K_2 = 1.0 \times 10^{-7}$ "

$K_3 = 1.3 \times 10^{-5}$ "

$K_4 = 9.0 \times 10^{-3}$ —

$K_5 = 5.9 \times 10^{1}$ —

Table III

FOURIER AMPLITUDES OF THE CONCENTRATIONS AT 10^{-6} SEC FOR THE HIGH TEMPERATURE AIR SYSTEM

Input Frequency	Rate Coefficient	Fourier Amplitude
$[O_2] \times 10^9$ moles/cc		
2	k_1	-4.47
90	k_5	-0.0244
74	k_4	-0.0227
42	k_2	-4.7×10^{-4}
62	k_3	-3.9×10^{-4}
$[O] \times 10^9$ moles/cc		
2	k_1	8.53
74	k_4	-0.36
90	k_5	0.018
62	k_3	-0.029
42	k_2	0.0027
$[N_2] \times 10^9$ moles/cc		
2	k_1	-0.389
74	k_4	-0.386

Table IV

FOURIER AMPLITUDES OF THE CONCENTRATIONS AT 10^{-4} SEC
FOR THE HIGH TEMPERATURE AIR SYSTEM

Input Frequency	Rate Coefficient	Fourier Amplitude
	$[O_2] \times 10^8$ moles/cc	
2	k_1	-1.1
90	k_5	-0.147
74	k_4	-0.087
62	k_3	-0.069
42	k_2	-0.044
	$[O] \times 10^8$ moles/cc	
2	k_1	2.17
62	k_3	0.228
90	k_5	0.164
42	k_2	0.078
74	k_4	-0.00146
	$[N_2] \times 10^9$ moles/cc	
74	k_4	-2.6
2	k_1	-2.3
62	k_3	-1.0

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Table V

Initial Conditions, the Rate Coefficients and Equilibrium Constants for the $H_2 - O_2$ Reaction

Initial Conditions

$$[H_2] = 8.0 \times 10^{-9} \text{ moles/cc}$$

$$[O_2] = 4.0 \times 10^{-9} \text{ moles/cc}$$

Rate Coefficients

$k_1^o = 5.78 \times 10^4 \text{ (moles/cc)}^{-1}\text{sec}^{-1}$ $\qquad$ $k_6^o = 4.0 \times 10^{13} \text{ (moles/cc)}^{-1}\text{sec}^{-1}$

$k_2^o = 4.47 \times 10^3$ " $\qquad\qquad$ $k_7^o = 1.51 \times 10^{13}$ "

$k_3^o = 1.03 \times 10^5$ " $\qquad\qquad$ $k_8^o = 2.20 \times 10^6$ "

$k_4^o = 6.79 \times 10^5$ " $\qquad\qquad$ $k_9^o = 1.6 \times 10^{14}$ "

$k_5^o = 1.23 \times 10^{12}$ "

Equilibrium Constants

$K_1 = 1.59 \times 10^{-11} \text{ moles/cc}$ $\qquad$ $K_6 = 1.4$ -

$K_2 = 2.69 \times 10^{-12}$ " $\qquad\qquad$ $K_7 = 9.76$ -

$K_3 = 1.14 \times 10^{-11}$ " $\qquad\qquad$ $K_8 = 2.02$ -

$K_4 = 1.63 \times 10^{-12}$ " $\qquad\qquad$ $K_9 = 6.76$ -

$K_5 = 2.37 \times 10^{-1}$ -

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Table VI

FOURIER AMPLITUDES OF THE CONCENTRATIONS AT 10^{-8} SEC FOR THE $H_2 - O_2$ REACTION

Rate Coefficient	Fourier Amplitude	Rate Coefficient	Fourier Amplitude
$[H_2]$.		$[O_2]$	
Insensitive to uncertainties in any rate constant.		Insensitive to uncertainties in any rate constant.	
$[H] \times 10^{19}$		$[O] \times 10^{20}$	
k_1	4.67	k_2	1.79
k_8	0.202	k_6	-0.016
k_7	0.202	k_1	0.0065
k_5	0.010	k_5	0.0065
k_6	0.0023	k_3	2.25×10^{-5}
k_2	0.00165	k_4	-1.95×10^{-5}
k_4	8.0×10^{-5}	k_9	7.87×10^{-6}
k_9	4.1×10^{-5}	k_8	1.20×10^{-6}
k_3	-3.0×10^{-5}	k_7	-8.46×10^{-7}
$[OH] \times 10^{18}$		$[H_2O] \times 10^{20}$	
k_8	5.9	k_8	2.03
k_7	-0.0203	k_7	2.03
k_9	0.00176	k_5	0.121
k_5	0.0014	k_6	0.0066
k_2	1.51×10^{-4}	k_4	8.35×10^{-4}
k_6	9.73×10^{-5}	k_1	-6.35×10^{-4}
k_1	7.08×10^{-5}	k_9	4.22×10^{-4}
k_4	-7.43×10^{-6}	k_3	-2.81×10^{-4}
k_3	3.13×10^{-6}	k_2	1.33×10^{-4}

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Table VII

FOURIER AMPLITUDES OF THE CONCENTRATIONS AT 10^{-3} SEC
FOR THE H_2 - O_2 REACTION.

Rate Coefficient	Fourier Amplitude	Rate Coefficient	Fourier Amplitude
$[H_2]$ x 10^9		$[H]$ x 10^9	
k_5	-3.71	k_5	1.92
k_7	-0.346	k_7	1.92
k_6	-0.313	k_6	0.122
k_8	-0.172	k_8	0.102
k_2	-0.108	k_2	0.061
k_4	-0.101	k_9	0.0466
k_9	-0.0905	k_4	0.0439
k_1	-0.0491	k_1	0.0176
k_3	0.0119	k_3	-0.00318
$[O_2]$ x 10^9		$[O]$ x 10^{10}	
k_5	-1.77	k_5	5.77
k_7	-0.153	k_7	0.420
k_6	-0.089	k_1	0.164
k_8	-0.070	k_6	0.162

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II. APPLICATIONS

1. R.I. Cukier, C.N. Fortuin, K.E. Shuler, A.G. Petschek and J.H. Schaibly, J. Chem. Phys.....(preceding paper)

2. C.W. Gear, "The Numerical Integration of Stiff Differential Equations," University of Illinois, Dept. of Computer Sciences, Report No.221, Jan. 1967.

3. The equilibrium constants were calculated from data in B.J. McBride, Thermodynamic Properties to 6000° K for 210 Substances Involving the First 18 Elements, NASA, SP-3001 (1963). The rate coefficients were taken from: J.C. Schexnayder and J.S. Evens, NASA Technical Report R-108, (1961); H.S. Glick, J.J. Klein, and W. Squire, J. Chem. Phys., 27, 850 (1957); G.B. Kistiakowski and G.C. Volpi, J. Chem. Phys. 27, 1141, (1957). We are aware that more recent "nominal" values of the various rate coefficients exist in the literature but feel that the values used in our calculations are adequate for the purpose of this paper.

4. The equilibrium constants were calculated from the data in McBride (see Ref.2.); the rate coefficients were obtained from the compilation of G.S. Bahn, Reaction Rate Compilation for the H-O-N System, Gordon and Breach Science Publishers, New York (1968).